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# The Effect of $B_2O_3$ Addition on the Direct Sintering of Barium Hexaferrite

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***Abstract***

*The effect of $B_2O_3$ on the calcination and on the material and magnetic properties of the direct-sintered isotropic hard barium ferrite $BaO.5.6Fe_2O_3$ was studied in the 0–0·2 mol $B_2O_3$ addition range. The addition of 0·01 mol $B_2O_3$ as boric acid in the milling stage of the raw materials, $BaCO_3$ and $Fe_2O_3$, resulted in the enhancement of the barium hexaferrite phase in calcinations below 1000°C. In the direct-sintering process, the optimum magnetic properties ($B_r$ = 2000–2300 Gauss, ${}_jH_C$ > 2500 Oersted, $(B.H)_{max}$ > 1 MG.Oe) were obtained with 0·01 and 0·05 mol $B_2O_3$ addition levels in the samples sintered at 1150°C for 2–3 h, and also in 0·05 mol $B_2O_3$ samples sintered at 1200 and 1250°C for 1 h. The $B_2O_3$ addition resulted in enhancement of the magnetic properties not only by aiding densification due to liquid-phase sintering, but at temperatures above 1100°C, by increasing the magnetic moment developed in the unit cell of the material. The optimum condition in this case was found to be the 0·05 mol $B_2O_3$ addition level.*

*Der Effekt des $B_2O_3$ auf die Kalzinierung und auf das Material und seine magnetischen Eigenschaften wurde für direktgesintertes, isotrop hartes Bariumferrit, $BaO.5.6Fe_2O_3$, für eine Zugabe von $B_2O_3$ zwischen 0 und 0·2 Mol untersucht. Die Zugabe von 0·01 Mol $B_2O_3$ zu den Rohmaterialien $BaCO_3$ und $Fe_2O_3$ in der Form von Borsäure während des Mahlprozesses ergab eine Steigerung der Bariumhexaferritphase bei Kalzinierung unterhalb von 1000°C. Beim Direktsinterprozeß ergaben sich die optimalen magnetischen Eigenschaften ($B_r$ = 2000–2300 Gauss, ${}_jH_C$ > 2500 Oersted, $(B.H)_{max}$ > 1 MG.Oe) bei einer Zugabe von 0·01 und 0·05 Mol $B_2O_3$ für Proben, die bei 1150°C für 2–3 h gesintert wurden, und bei Zugabe von 0·05 Mol $B_2O_3$ für Sintertemperaturen von 1200 und 1250°C und Sinterzeiten von 1 h. Die $B_2O_3$-Zugabe ergab eine Steigerung der magnetischen Eigenschaften nicht allein durch die erhöhte Dichte infolge einer Flüssigphasensinterung sondern, bei Temperaturen oberhalb von 1100°C, durch eine Erhöhung des magnetischen Moments der Einheitszelle des Materials. In diesem Fall lag die optimale $B_2O_3$-Zugabe bei 0·05 Mol.*

*L'objectif de cette étude a été d'étudier l'effet de $B_2O_3$ sur la calcination et le frittage de la ferrite de barium isotropique dure exprimée par la formule $BaO.5.6Fe_2O_3$, dans l'intervalle de 0 à 0·2 mol. L'addition de 0·01 mol de $B_2O_3$ comme acide borique pendant le broyage de $BaCO_3$ et de $Fe_2O_3$ a augmenté la formation de la phase barium hexaferrite pour les calcinations au-dessous de 1000°C. Au frittage direct, les propriétés magnétiques optima ($B_r$ = 2000–2300 Gauss, ${}_jH_C$ > 2500 Oersted, $(B.H)_{max}$ > 1 MG.Oe) ont été obtenues pour les échantillons à 0·01 et 0·05 mol $B_2O_3$ frittés 2–3 h à 1150°C et pour les échantillons à 0·05 mol $B_2O_3$ frittés 1 h à 1200 et 1250°C. L'addition de $B_2O_3$ améliore les propriétés magnétiques en augmentant la densité par formation d'une phase liquide et pour les frittages au-dessus de 1100°C en augmentant le moment magnétique du réseau cristallin. La condition optimum est obtenue dans ce cas pour une addition de 0·05 mol $B_2O_3$.*



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## 1 Introduction

The processing of magnetically hard ceramic materials dates back to the early fifties. The opinion expressed at the time was that these materials, now known as hard ferrites, were of great economic importance as an alternate cheap source of magnetomotive force to alloy magnets. This has been fully confirmed.[1]

The general composition of hard ferrites, also referred to as 'hexagonal ferrites', is expressed as $MeO.6Fe_2O_3$. In the formula, Me represents the divalent ions like $Ba^{2+}$, $Sr^{2+}$, $Pb^{2+}$ or a mixture of them. According to the magnetic properties, hard ferrites are grouped into two categories termed 'isotropic' and 'anisotropic' ferrites. In the isotropic case, the material shows equal magnetic properties in all material directions, due to the random orientation of the *c*-axis of the grains, which is the easy magnetization direction. The value of remanent magnetization ($B_r$) in these ferrites is in the order of 2000 Gauss and the coercive force ($H_c$) ranges from 1500 to 20 000 Oersted depending on the processing of the material. In anisotropic hard ferrites, enhanced remanent magnetization in one direction of the material is obtained by orientating the *c*-axis of the plate-like hexagonal ferrite crystals to the direction of an external high magnetic field applied during the shaping process of the material. Such ferrites develop, remanent magnetization nearly twice the value of the isotropic ones.[1,2]

Isotropic hard ferrites are produced according to the conventional ceramic processing technique. The method involves the following steps: wet milling of water insoluble ingredients in steel containers using steel balls, drying the mixture and calcination, regrinding and redrying the calcined product, granulation with a binder, pressing to the desired shape and finally sintering. In the formulations, usually less $Fe_2O_3$ than the stoichiometric proportion is used due to the iron pickup during the milling operations.

Since the fifties a great number of advances have been made in the chemistry, in the manufacturing techniques and in the application of both isotropic and anisotropic hard ferrites. Most of the early research was focused on the special additives for improving the magnetic properties of the material. In particular, the addition of $Ca^{2+}$ in Ba and Sr hexaferrite was found to be important in achieving high reactivity in sintering and in increasing the coercive force.[3] Various fluxing or crystal growth inhibiting agents such as $SiO_2$, $Al_2O_3$, PbO and $B_2O_3$ have also been found to be useful as additives for obtaining the desired structural and magnetic properties in the ferrites.[4–6] Among these additives $B_2O_3$ has engendered special attention.[7–8] Hung and coworkers have investigated the effect of a 0·01–0·07 mol $B_2O_3$ addition on the magnetic properties of both isotropic and aniso-tropic hard ferrites and found that optimum properties developed at about 0·03 mol due to the enhanced densification resulting from liquid-phase sintering.[6] In all these investigations, a calcination step has been employed in the processing of the material.

The present research, therefore, aims at studying the effect of $B_2O_3$ additions over a wider spectrum on the formation of the hexaferrite phase during the calcination process and also its possible application in the production of isotropic ferrites by direct sintering of the raw materials.

## 2 Experimental

The basic formula of $BaO.5{\cdot}6Fe_2O_3$ was used throughout the study. Pure grade barium carbonate (>99·5% purity, Merck, Germany) and indigenous hematite (>99·7% purity, EVA A.Ş., Turkey) were weighed according to the formulation. The raw materials were then ball-milled in deionized water at 60 rpm for 8 h, using a 3 litre capacity steel jar and steel cylindrical balls of 2 cm diameter 3 cm length.

In the milling operations, 1 wt% PVA and the calculated amount of boric acid were added to yield 0·01, 0·05, 0·1, 0·15 and 0·2 mol $B_2O_3$. After drying the mixtures to 10% humidity, the powders were granulated to ~150 $\mu$m. From the granulated powders, cylindrical samples of 16 mm diameter, 8 mm thickness were pressed at 30 MPa. These samples were then calcined in a furnace at 750, 800, 850, 900, 950 and 1000°C for 1 h, using a 200°C/h heating rate. The calcined samples were tested by X-ray diffraction using Co $K_\alpha$ radiation to determine the unreacted $Fe_2O_3$ phase.

To study the direct-sintering method, specimens of the previously mentioned dimensions were pressed in a floating die system at a pressure of 100 MPa to a green density of $2{\cdot}7 \times 10^3$ kg/m$^3$. The sintering was carried out at 1100 and 1150°C for 1–4 h and at 1200 and 1250°C 1 h, in a furnace with atmospheric conditions, employing again a 200°C/h heating rate and then self-cooling. The microstructures of the samples were studied in a Jeol 840 scanning electron microscope. The bulk densities were determined from the mass and the measured volume ratio and the magnetic properties were obtained in permagraph equipment by Magnet-Physik (Köln, Germany).

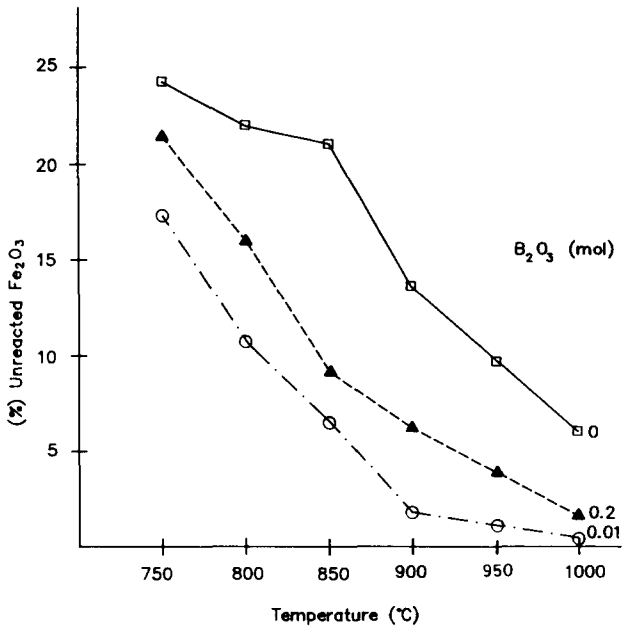


**Fig. 1.** The effect of $B_2O_3$ on the formation of the barium hexaferrite phase.

## 3 Results and discussions

### 3.1 The effect of the $B_2O_3$ addition on the calcination

The amount of unreacted $\alpha$-$Fe_2O_3$ in the calcined samples was calculated semi-quantitatively from the ratio of the maximum intensity diffraction peaks of $\alpha$-$Fe_2O_3$ ($d_{(104)}$ = 2·70 Å) to that of the barium hexaferrite ($d_{(107)}$ = 2·78 Å).

Figure 1 shows the variation of the unreacted $\alpha$-$Fe_2O_3$ phase at different calcination temperatures in the samples containing 0, 0·01 and 0·2 mol of $B_2O_3$. To avoid crowding in the figure, the results of the other $B_2O_3$ additions were not shown, since their values lay between that of 0·01 and 0·2 mol. The results show that $B_2O_3$ addition promotes the formation of the barium hexaferrite phase over the studied range of calcination temperatures. The maximum effect was obtained with the minimum $B_2O_3$ sample. The results are considered to be important for the production of isotropic and anisotropic hard ferrites since the usual calcination temperature employed (1000–1100°C) could be lowered to 800–850°C with 0·01 mol $B_2O_3$ addition to the formulations.

### 3.2 Bulk density and the microstructure of the direct-sintered samples

In Fig. 2, the bulk densities of the direct-sintered samples, at 1100 and 1150°C for 1–4 h are given respectively. The bulk density of the samples sintered for 1 h at different temperatures are also compared in Fig. 3. In Figs 4 and 5, a series of secondary electron micrographs of the fracture surface are given for the samples containing different $B_2O_3$ additions sintered at 1100 and 1200°C for 1 h respectively.

The powder densities of the sintered samples (ground to ~35 $\mu$m) were measured using the picnometer method, employing distilled water as the displacement liquid. Variations between 4·83 × $10^3$ and 4·85 × $10^3$ kg/m$^3$ were obtained independent of the $B_2O_3$ contained in the samples. Hence the figure of 4·84 × $10^3$ kg/m$^3$ was accepted as the nearest figure for the theoretical density of the formulations.

In direct sintering the sample without any $B_2O_3$ at

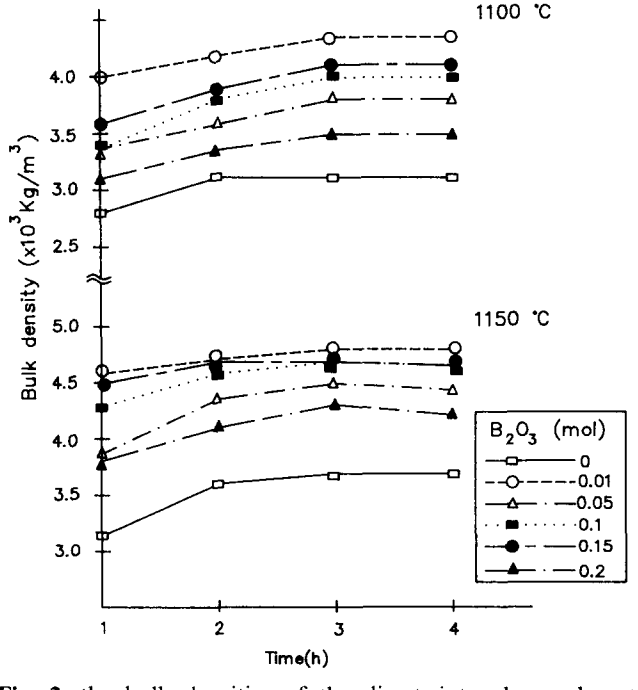


**Fig. 2.** the bulk densities of the direct-sintered samples at 1100 and 1150°C for 1–4 h.

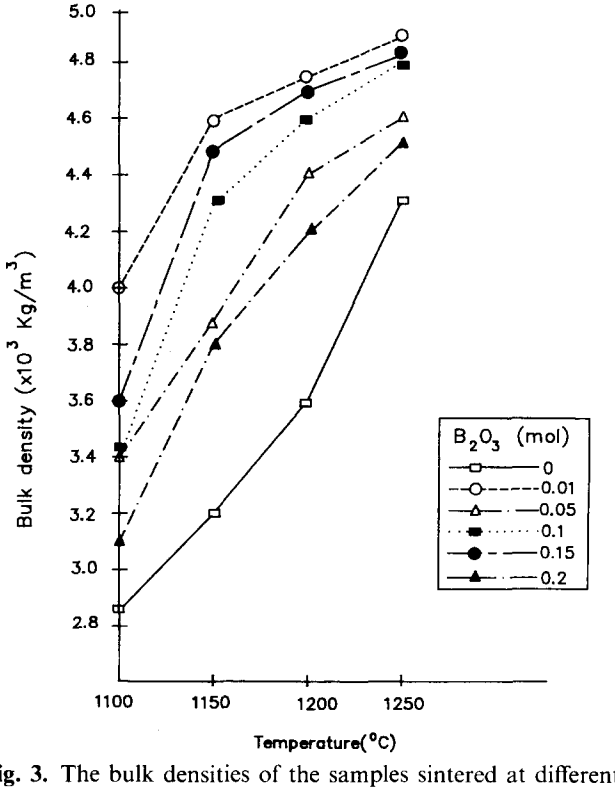


**Fig. 3.** The bulk densities of the samples sintered at different temperatures for 1 h.

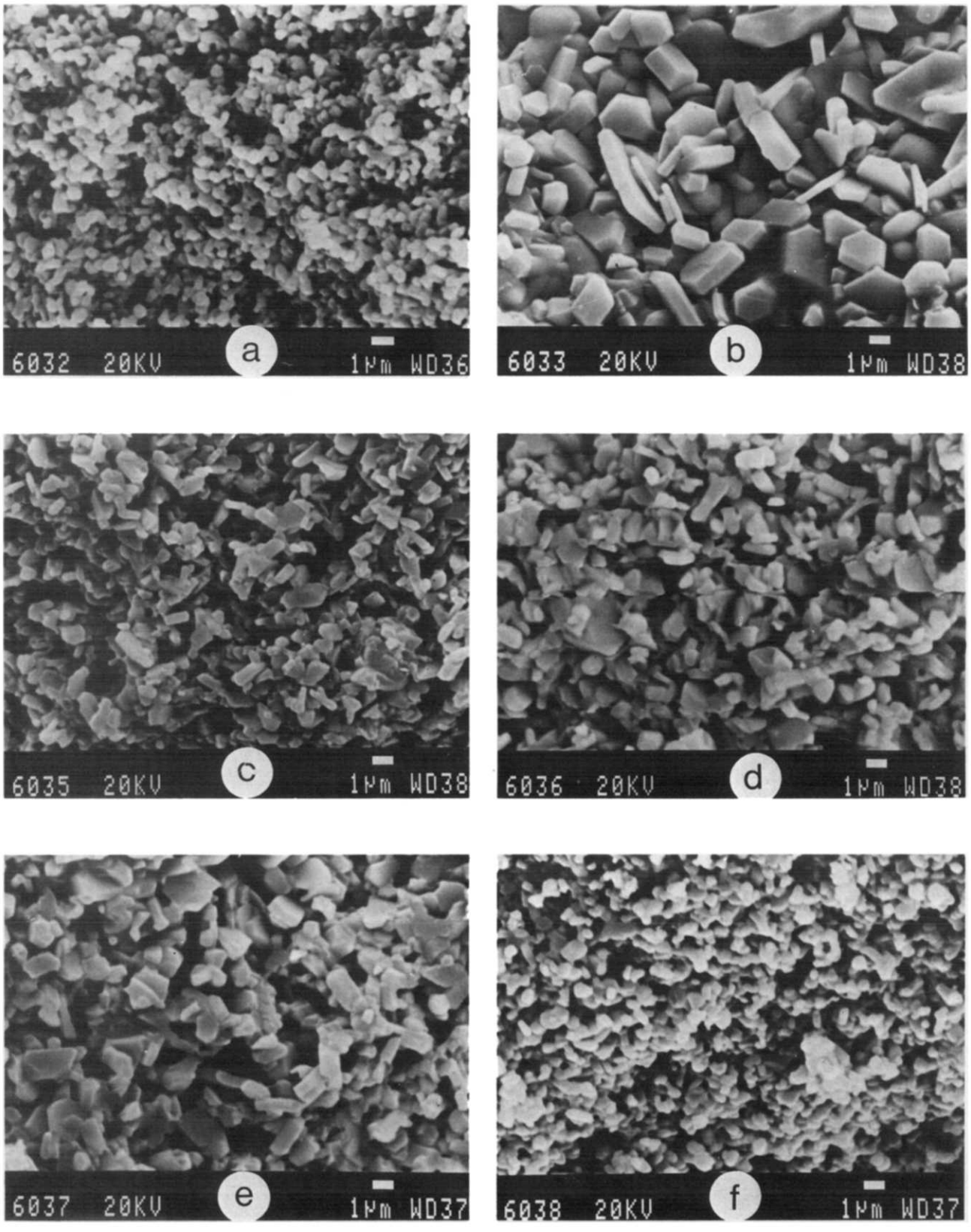


**Fig. 4.** The secondary electron micrographs of the samples sintered at 1100°C, (a) 0 mol $B_2O_3$, (b) 0·01 mol $B_2O_3$, (c) 0·05 mol $B_2O_3$, (d) 0·1 mol $B_2O_3$, (e) 0·15 mol $B_2O_3$, (f) 0·2 mol $B_2O_3$.

1100°C for 1 h, a low bulk density of $2{\cdot}8 \times 10^3$ kg/m$^3$ was obtained which was slightly higher than the green density ($2{\cdot}7 \times 10^3$kg/m$^3$). This sample showed a fine-grained (<1 $\mu$m), highly porous microstructure (Fig. 4(a)). In prolonged sintering at this temperature, the bulk density of the sample reached only $3{\cdot}0 \times 10^3$ kg/m$^3$ which is about 64% of the theoretical density value. However, the addition of 0·01 mol $B_2O_3$ resulted in a sudden rise in the bulk density to a figure of $4{\cdot}0 \times 10^3$ kg/m$^3$. The prolonged firing increased this figure further to $4{\cdot}4 \times 10^3$, which is 91% of the theoretical

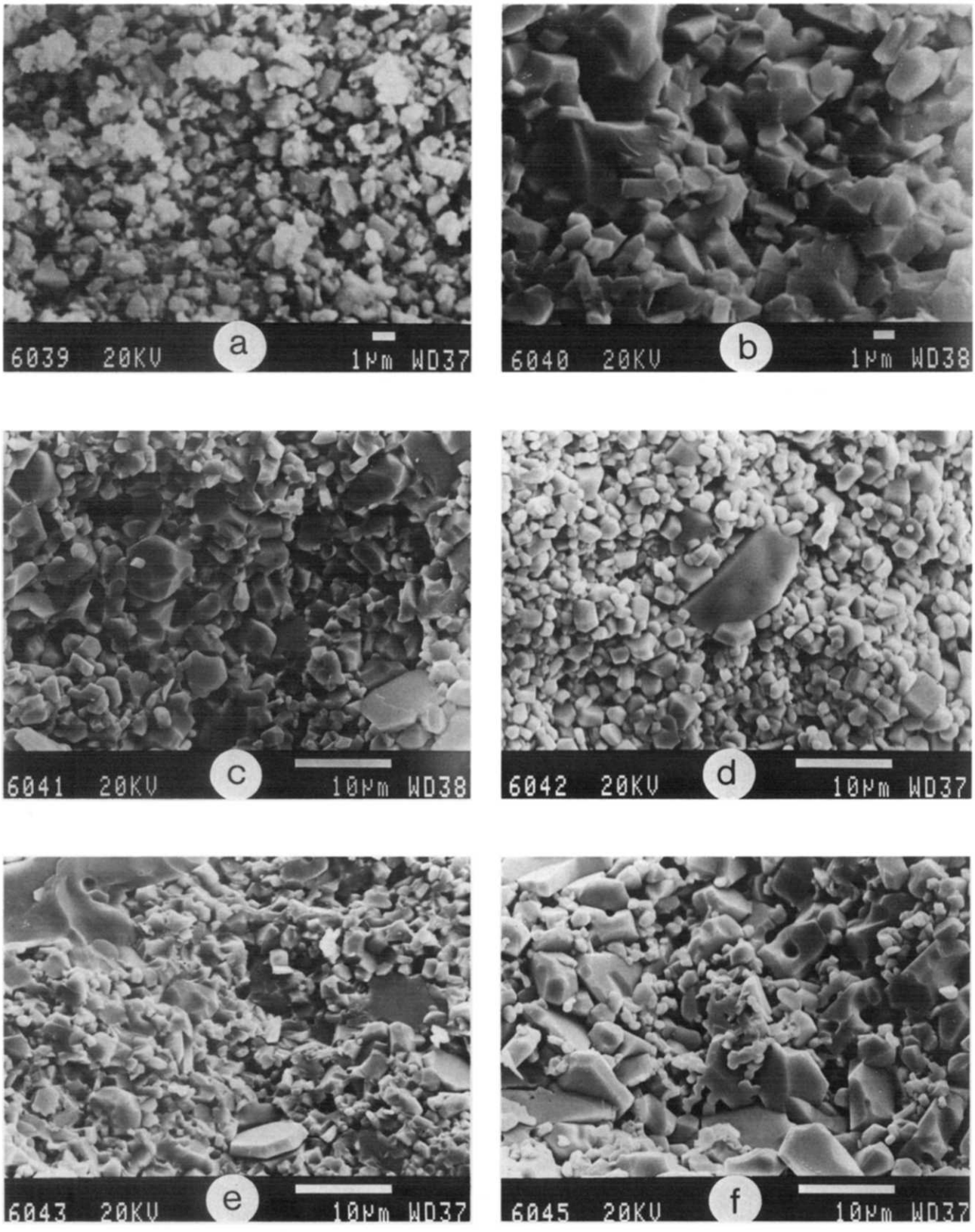


**Fig. 5.** The secondary electron micrographs of the samples sintered at 1200°C, (a) 0 mol $B_2O_3$, (b) 0·01 mol $B_2O_3$, (c) 0·05 mol $B_2O_3$, (d) 0·1 mol $B_2O_3$, (e) 0·15 mol $B_2O_3$, (f) 0·2 mol $B_2O_3$.

value. The microstructure of this sample showed well-formed hexagonal plate-like grains of quite uniform size (Fig. 4(b)).

In contrast to this result, the addition of 0·05 mol $B_2O_3$ resulted in a low bulk density, giving a fine-grained porous microstructure (Fig. 4(c)). Although the further addition of $B_2O_3$ up to 0·15 mol raised the bulk density, the figures obtained were below that of the 0·01 mol $B_2O_3$ added sample. A correspondingly slight increase in grain size was observed in these samples compared to the $B_2O_3$-free sample (Fig. 4(d) and

(e)). When the addition of $B_2O_3$ was raised to 0·2 mol, again a sudden lowering in the bulk density was obtained, hence resulting in a porous and fine-grained microstructure (Fig. 4(f)).

A similar variation in the bulk densities was also observed in the direct-sintered samples at 1150°C and at 1200°C (Figs 2 and 3). The highest densification again observed in 0·01 mol $B_2O_3$ samples reached 95 and 99% of the theoretical value respectively. The microstructures of the samples sintered at 1200°C (Fig. 5(a)–(f), in general, the densification and grain growth levels obtained. An important observation at this temperature was the loss of the well-formed hexagonal crystalline structure in the 0·01 mol $B_2O_3$ added sample and the start of discontinuous grain growth in the high $B_2O_3$ added samples. However, at 1250°C sintering, the densification in the 0·1 and 0·15 mol $B_2O_3$ added samples were found to be higher than the 0·01 mol $B_2O_3$ added samples.

The lowering of the bulk densities with increasing amount of $B_2O_3$ addition (0·01–0·07 mol range) at fixed sintering temperature was also observed by Hung *et al.*[6] Although the reason for this was not discussed, liquid-phase sintering was proposed as the densification mechanism. They also suggested that the substitution of $B^{3+}$ ions for the $Fe^{3+}$ in the tetrahedral sites of the structure could also take place with $B_2O_3$ additions below 0·3 mol. If, as suggested, liquid-phase sintering is the main factor governing densification, the low bulk density figures obtained in the 0·05 and 0·2 mol $B_2O_3$ added samples can not be explained by this model only. The X-ray diffraction study on the sintered samples did not reveal the presence of a second phase within the detection limits of the technique. The formation of hexagonal plate-like structures in the 0·01 mol $B_2O_3$ added sample sintered at 1100°C for 1 h points either to a different densification model or to a complicated liquid-phase sintering mechanism. As mentioned in the previous section a detailed study is therefore required in the related phase systems to elucidate the exact nature of the mechanism.[9–11]

### 3.3 The effect of $B_2O_3$ on the magnetic properties of direct-sintered samples

In Figs 6 and 7, the remanent magnetization ($B_r$), intrinsic coercivity ($_jH_c$) and $(B.H)_{max}$ of the samples sintered at 1100 and 1150°C for 1–4 h are shown respectively. The same properties of the samples sintered at different temperatures for 1 h are also compared in Fig. 8.

The value of $B_r$ in an isotropic barium hexaferrite depends not only on the strength of the magnetic dipole moment developed in the unit cell, but also on the degree of densification attained

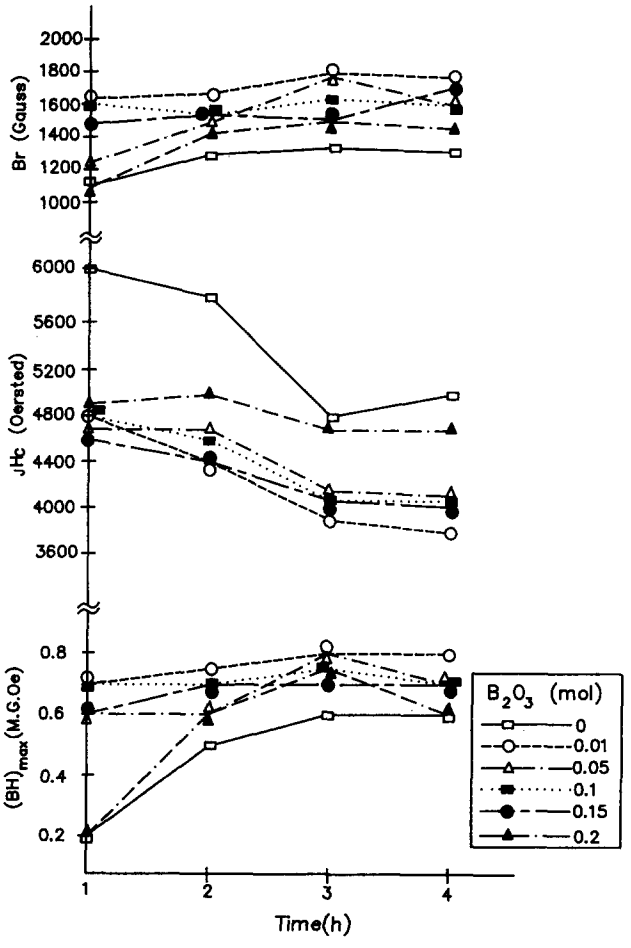


**Fig. 6.** The magnetic properties of the direct-sintered samples at 1100°C for 1–4 h.

during sintering of the material. On the other hand, the coercive force of the ferrite is strongly dependent on the grain size developed during the sintering. As the grain size is reduced, the coercive force increases and it reaches a limiting value when the grain size approaches the size of a single domain.

The measured magnetic values of the samples containing different $B_2O_3$ additions, sintered at 1100°C for 1–4 h, follow this argument very closely. Thus the sample without any $B_2O_3$ addition, which had the lowest bulk density and finest grained microstructure, gave the lowest $B_r$ and highest $_jH_C$ values. Although the 0·01 mol $B_2O_3$ added sample showed a large and well-formed hexagonal plate-like microstructure when sintered at 1100°C for 1 h, the thickness of the plates in the *c*-direction and the direction of easy magnetization were comparable to the grain size of the other $B_2O_3$ added samples. Hence the coercivity values obtained in these samples are very close (Fig. 4 (b)–(f) and Fig. 6). However, the overall magnetic values obtained in sinterings at this temperature were below the desired values from an isotropic hard ferrite.

In contrast to these results, in prolonged sinterings at 1150°C, the samples having more than 0·01 mol $B_2O_3$ gave better remanent magnetization

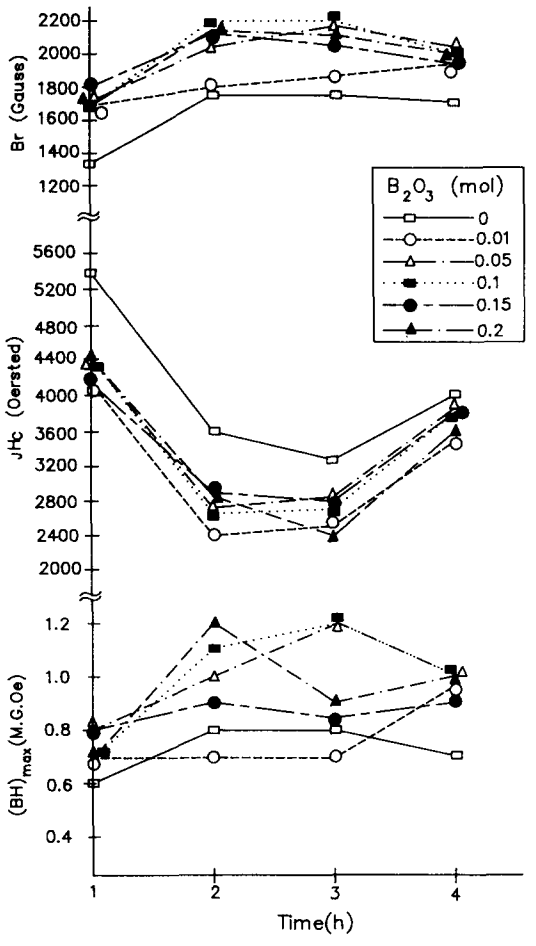


**Fig. 7.** The magnetic properties of the direct-sintered samples at 1150°C for 1–4 h.

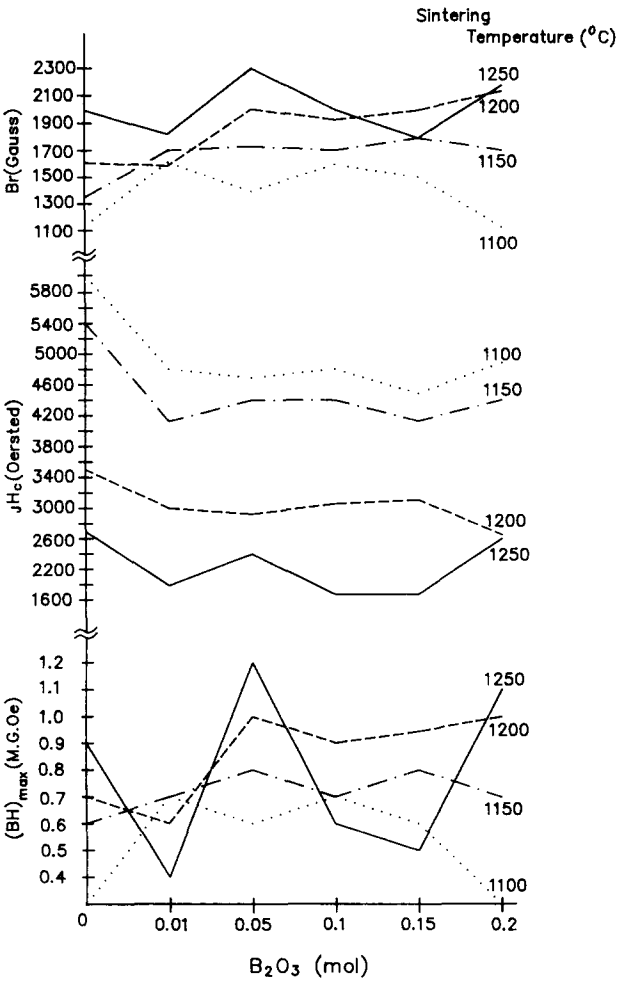


**Fig. 8.** The magnetic properties of the samples sintered at different temperatures for 1 h.

values, though they had lower bulk densities. The optimum values were obtained in the 0·05 and 0·1 mol $B_2O_3$ added samples, giving $B_r$ and $(B.H)_{max}$ as 2200 Gauss and 1·2 MG.Oe respectively, which were higher than the figures normally quoted for the isotropic barium ferrite produced by the conventional ceramic production technique involving the calcination step.

Similar magnetic values were obtained in the 0·05 mol $B_2O_3$ added sample sintered at 1200°C for 1 h. This sample yielded the highest $B_r$ value measured (2300 Gauss) when sintered at 1250°C for 1 h (Fig. 8). However, at this temperature the 0·1 and 0·15 mol $B_2O_3$ added samples gave poor $B_r$ and $(B.H)_{max}$ values, which again rose to a reasonable level in the 0·2 mol $B_2O_3$ added samples. These observations indicate that the $B_2O_3$ addition to barium hexaferrite results in an increase in $B_r$ values not only by promoting the densification by liquid-phase sintering, but at high sintering temperatures it also increases the magnetization developed in the unit cell of the material, the optimum being at the 0·5 mol $B_2O_3$ addition level. This figure is in close agreement with the figure of 0·03 mol quoted by Hung *et al.* as the possible substitution level of $B^{3+}$ ions in the tetrahedral interstices of the hexaferrite lattice.

## 4 Conclusions

(1) The addition of 0·01 mol $B_2O_3$ as boric acid to the milled raw materials in the production of barium hard ferrite aids in the formation of barium hexaferrite phase. Therefore, a lower calcination temperature (800°C) can be utilized in the conventional processing of the material.

(2) Isotropic hard barium ferrite with good magnetic properties ($B_r$ = 2000–2300 Gauss, ${}_JH_C$ > 2500 Oersted, $(B.H)_{max}$ > 1 MG.Oe) can be produced by the direct sintering of $B_2O_3$-doped raw materials. These magnetic properties can be obtained at the 0·01 and 0·05 mol $B_2O_3$ addition level in sintering at 1150°C for 2 h, and also at the 0·05 mol $B_2O_3$ addition level in sintering at 1200 and 1250°C for 1 h.

(3) The addition of $B_2O_3$ enhances the magnetic properties not only by aiding densification by possible liquid-phase sintering, but at temperatures above 1100°C it also increases the magnetic dipole moment developed in the unit cell of the material. The optimum condition in this case was found to be at the 0·05 mol $B_2O_3$ addition level.

(4) In sintering at 1100°C for 1 h, and 0·01 mol $B_2O_3$ addition results in the formation of plate-like well-defined hexagonal grains which give potential utilization for the production of the anisotropic materials.

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